METHOD 8321B

SOLVENT-EXTRACTABLE NONVOLATILE COMPOUNDS BY HIGH PERFORMANCE LIQUID CHROMATOGRAPHY/THERMOSPRAY/MASS SPECTROMETRY (HPLC/TS/MS) OR ULTRAVIOLET (UV) DETECTION

1.0 SCOPE AND APPLICATION

1.1 This method covers the use of high performance liquid chromatography (HPLC), coupled with both thermospray-mass spectrometry (TS-MS) and an ultraviolet (UV) detector, for the determination of disperse azo dyes, organophosphorus compounds, tris(2,3-dibromopropyl) phosphate, chlorinated phenoxyacid compounds and their esters, and carbamates in wastewater, ground water, and soil/sediment matrices. Data are also provided for the determination of chlorophenoxy acid herbicides in fly ash (Table 12), however, recoveries for most compounds are very low, indicating poor extraction efficiency for these analytes using the extraction procedure included in this method. The following compounds may be determined by this method, although not all of the compounds are amenable to UV detection:

Analyte	CAS No.
Azo Dyes	
Disperse Red 1	2872-52-8
Disperse Red 5	3769-57-1
Disperse Red 13	126038-78-6
Disperse Yellow 5	6439-53-8
Disperse Orange 3	730-40-5
Disperse Orange 30	5261-31-4
Disperse Brown 1	17464-91-4
Solvent Red 3	6535-42-8
Solvent Red 23	85-86-9
Anthraquinone Dyes	
Disperse Blue 3	2475-46-9
Disperse Blue 14	2475-44-7
Disperse Red 60	17418-58-5
Coumarin Dyes	
Fluorescent Brighteners	
Fluorescent Brightener 61	8066-05-5
Fluorescent Brightener 236	3333-62-8
Alkaloids	
Caffeine	58-08-2

Analyte	CAS No.
Strychnine	57-24-9
Organophosphorus Compounds	
Methomyl	16752-77-5
Thiofanox	39196-18-4
Famphur	52-85-7
Asulam	3337-71-1
Dichlorvos	62-73-7
Dimethoate	60-51-5
Disulfoton	298-04-4
Fensulfothion	115-90-2
Merphos	150-50-5
Parathion methyl	298-00-0
Monocrotophos	6923-22-4
Naled	300-76-5
Phorate	298-02-2
Trichlorfon	52-68-6
Tris(2,3-dibromopropyl) phosphate (Tris-BP)	126-72-7
Chlorinated Phenoxyacid Compounds	
Dalapon	75-99-0
Dicamba	1918-00-9
2,4-D	94-75-7
MCPA	94-74-6
MCPP	7085-19-0
Dichlorprop	120-36-5
2,4,5-T	93-76-5
Silvex (2,4,5-TP)	93-72-1
Dinoseb	88-85-7
2,4-DB	94-82-6
2,4-D, butoxyethanol ester	1929-73-3
2,4-D, ethylhexyl ester	1928-43-4
2,4,5-T, butyl ester	93-79-8
2,4,5-T, butoxyethanol ester	2545-59-7
Carbamates	
Aldicarb*	116-06-3

Analyte	CAS No.
Aldicarb sulfone	1646-88-4
Aldicarb sulfoxide	1646-87-3
Aminocarb	2032-59-9
Barban	101-27-9
Benomyl	17804-35-2
Bromacil	314-40-9
Bendiocarb*	22781-23-3
Carbaryl*	63-25-2
Carbendazim*	10605-21-7
3-Hydroxycarbofuran	16655-82-6
Carbofuran*	1563-66-2
Chloroxuron	1982-47-4
Chloropropham	101-21-3
Diuron*	330-54-1
Fenuron	101-42-8
Fluometuron	2164-17-2
Linuron*	330-55-2
Methiocarb	2032-65-7
Methomyl*	16752-77-5
Mexacarbate	315-18-4
Monuron	150-68-5
Neburon	555-37-3
Oxamyl*	23135-22-0
Propachlor	1918-16-7
Propham	122-42-9
Propoxur	114-26-1
Siduron	1982-49-6
Tebuthiuron	34014-18-1

[a] Chemical Abstract Service Registry Number.
* These carbamates were tested in a multi-laboratory evaluation. All others were tested in a single-laboratory evaluation.

1.2 This method may be applicable to the analysis of other non-volatile or semivolatile compounds that are solvent-extractable, are amenable to HPLC, and can be ionized under thermospray introduction for mass spectrometric detection or can be determined by a UV detector.

1.3 Method 8321 is designed to detect the chlorinated phenoxyacid compounds (free acid form) and their esters without the use of hydrolysis and esterification in the extraction procedure, although hydrolysis to the acid form will simplify quantitation.

1.4 The compounds listed in this method were chosen for analysis by HPLC/MS because they have been designated as problem compounds that are hard to analyze by gas chromatographic methods. The sensitivity of this method is dependent upon the level of interferants within a given matrix, and varies with compound class and even by compound within a class. Additionally, the sensitivity is dependent upon the mode of operation of the mass spectrometer, with the selected reaction monitoring (SRM) mode providing greater sensitivity than single quadrupole scanning.

1.5 For further compound identification, MS/MS (CAD - Collision Activated Dissociation) can be used as an optional extension of this method.

1.6 Tris-BP has been classified as a carcinogen. Purified standard material and stock standard solutions should be handled in a hood.

1.7 This method is restricted to use by, or under the supervision of, analysts experienced in the use of high performance liquid chromatography using mass spectrometers or ultraviolet detectors. Analysts should also be skilled in the interpretation of liquid chromatograms and mass spectra. Each analyst must demonstrate the ability to generate acceptable results with this method.

2.0 SUMMARY OF METHOD

2.1 This method provides reversed-phase high performance liquid chromatographic (RP/HPLC) and thermospray (TS) mass spectrometric (MS) conditions and ultraviolet (UV) conditions for the detection of the target analytes.

2.1.1 Sample extracts can be analyzed by direct injection into the thermospray or onto a liquid chromatographic-thermospray interface

2.1.2 A gradient elution program is used on the chromatograph to separate the compounds.

2.1.3 Quantitative analysis may be performed by either TS/MS or UV detection, using either an external or internal standard approach. TS/MS detection may be performed in either a negative ionization (discharge electrode) mode or a positive ionization mode, with a single quadrupole mass spectrometer.

2.1.4 In some cases, the thermospray interface may introduce variability that leads to less precise quantitation. In such instances, the MS response may be used to identify the analytes of interest while the quantitative results are derived from the response of the UV detector.

2.2 Prior to analysis, appropriate sample preparation techniques must be used.

2.2.1 Samples for analysis of chlorinated phenoxyacid compounds may be prepared by a modification of Method 8151 (see Sec. 7.3) or other appropriate extraction technique. In general, the pH of a 1-L aqueous sample or 50-g solid sample is adjusted and

the sample is extracted with diethyl ether, concentrated, and the solvent exchanged to acetonitrile. Samples for these analytes may also be extracted using solid-phase extraction after a pH adjustment, as described in Method 3535.

2.2.2 For carbamates, 1-L aqueous samples or 40-g solid samples are extracted with methylene chloride (refer to appropriate 3500 series method), concentrated (preferably using a rotary evaporator with adapter) and the solvent exchanged to methanol.

2.2.3 Samples for analysis of the other target analytes are prepared by established extraction techniques. In general, water samples are extracted at a neutral pH with methylene chloride, using an appropriate 3500 series method. Solid samples are extracted with a mixture of methylene chloride/acetone (1:1), using an appropriate 3500 series method. Extract may require concentration and solvent exchange prior to analysis.

2.2.4 A micro-extraction technique for the extraction of Tris-BP from aqueous and non-aqueous matrices is included in this method (see Sec. 7.2).

2.3 An optional thermospray-mass spectrometry/mass spectrometry (TS-MS/MS) confirmatory procedure is provided in this method (see Sec. 7.11). That procedure employs MS/MS Collision Activated Dissociation (CAD) or wire-repeller CAD.

3.0 INTERFERENCES

3.1 Refer to Methods 3500, 3600, 8000 and 8151.

3.2 The use of Florisil Column Cleanup (Method 3620) has been demonstrated to yield recoveries less than 85% for some of the compounds in this method, and is therefore not recommended for all compounds. Refer to Table 2 of Method 3620 for recoveries of organophosphorus compounds as a function of Florisil fractions.

3.3 Compounds with high proton affinity may mask the MS response of some of the target analytes. Therefore, except when the thermospray MS/MS system is used for rapid screening of samples (see Sec. 7.11.1), an HPLC must be used to perform the chromatographic separations necessary for quantitative analyses.

3.4 Analytical difficulties encountered with specific organophosphorus compounds, as applied in this method, may include, but are not limited to, the following:

3.4.1 Methyl parathion shows some minor degradation during analysis.

3.4.2 Naled can undergo debromination to form dichlorvos. This reaction may occur during sample preparation and extraction, and the extent may depend of the nature of the sample matrix. The analyst should consider the potential for debromination of Naled when this compound is to be determined.

3.4.3 Merphos often contains contamination from merphos oxide. Oxidation of merphos can occur during storage, and possibly upon introduction into the mass spectrometer.

3.4.4 The water solubility of dichlorvos (DDVP) is 10 g/L at 20°C, and as a result, recovery of the this compound by solvent extraction from aqueous solutions is poor.

3.4.5 Trichloron rearranges and undergoes dehydrochlorination (loss of HCl) in acidic, neutral, or basic media, forming dichlorvos (DDVP). When either of these compounds are to be determined, the analyst should be aware of the possibility of this rearrangement in order to prevent misidentifications.

3.5 The chlorinated phenoxy acid compounds, being strong organic acids, react readily with alkaline substances and may be lost during analysis. Therefore, glassware and glass wool must be acid-rinsed, and sodium sulfate must be acidified with sulfuric acid prior to use, to avoid this possibility.

3.6 Due to the reactivity of the chlorinated herbicides, the standards must be prepared in acetonitrile. Methylation will occur slowly, if prepared in methanol.

3.7 Benomyl quickly degrades to carbendazim in the environment (Reference 21).

3.8 Solvents, reagents, glassware, and other sample processing hardware may yield discrete artifacts or elevated baselines, or both, causing misinterpretation of chromatograms or spectra. All of these materials must be demonstrated to be free from interferences under the conditions of the analysis by running reagent blanks. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be required.

3.9 Interferants co-extracted from the sample will vary considerably from source to source. Retention times of target analytes must be verified by using reference standards.

3.10 The optional use of HPLC/MS/MS methods aids in the confirmation of specific analytes. These methods are less subject to chemical noise than other mass spectrometric methods.

4.0 APPARATUS AND MATERIALS

4.1 HPLC/MS

The following apparatus and materials are necessary for the use of the HPLC/MS portions of this method.

4.1.1 High performance liquid chromatograph (HPLC) - An analytical system with programmable solvent delivery system and all required accessories, including injection loop (with a minimum 10-µL loop volume), analytical columns, purging gases, etc. At a minimum, the solvent delivery system must be capable of delivering a binary solvent system. The chromatographic system must be capable of being interfaced with a mass spectrometer (MS).

4.1.2 HPLC post-column addition pump - If post-column addition of reagents is employed, a pump is required. Ideally, this pump should be a syringe pump, and does not have to be capable of solvent programming. It is also possible to add the ionization reagents to the solvents and not perform post-column addition (see Sec. 7.6).

4.1.3 HPLC/MS interface

4.1.3.1 Interface - Thermospray ionization interface and source that will give acceptable calibration response for each analyte of interest at the concentration required. The source must be capable of generating both positive and negative ions, and have a discharge electrode or filament.

4.1.3.2 Micromixer - 10-µL, connects HPLC column system with HPLC post-column addition solvent system, if post-column addition is used.

4.1.4 Mass spectrometer system

4.1.4.1 A single quadrupole mass spectrometer capable of scanning from 1 to 1000 amu. The spectrometer must also be capable of scanning from 150 to 450 amu in 1.5 sec. or less, using 70 volts (nominal) electron energy in the positive or negative electron impact modes. In addition, the mass spectrometer must be capable of producing a calibrated mass spectrum for PEG 400, 600, or 800 (see Sec. 5.14) or other compounds used for mass calibration.

4.1.4.2 Optional triple quadrupole mass spectrometer - capable of generating daughter ion spectra with a collision gas in the second quadrupole and operation in the single quadrupole mode.

4.1.5 Data system - A computer system that allows the continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the duration of the chromatographic program must be connected to the mass spectrometer. The computer must have software that allows any MS data file to be searched for ions of a specified mass, and such ion abundances to be plotted versus time or scan number. This type of plot is defined as an Extracted Ion Current Profile (EICP). Software must also be available that allows integration of the abundances in any EICP between specified time or scan-number limits. There must be computer software available to operate the specific modes of the mass spectrometer.

4.2 HPLC with UV detector

An analytical system with solvent programmable pumping system for at least a binary solvent system, and all required accessories including syringes, 10-µL injection loop, analytical columns, purging gases, etc. An automatic injector is optional, but is useful for multiple samples. The columns specified in Sec. 4.3 are also used with this system.

If the UV detector is to be used in tandem with the thermospray interface, then the detector cell must be capable of withstanding high pressures (up to 6000 psi). However, the UV detector may be attached to an HPLC independent of the HPLC/TS/MS and, in that case, standard HPLC pressures are acceptable.

4.3 HPLC columns - A guard column and an analytical column are necessary.

The columns listed in this section were those used to develop the method. The mention of these columns is not intended to exclude the use of other columns that are available or that may be developed. Laboratories may use columns of other dimensions and/or packed with different stationary phases, provided that they document method performance data (e.g., chromatographic

resolution, analyte breakdown, and quantitation limits) that provide analytical performance that is appropriate for the intended application.

4.3.1 Guard Column - C_{18} reversed-phase guard column, 10 mm x 2.6 mm ID, 0.5-µm frit, or equivalent. The guard column should be packed with the same or similar stationary phase as the analytical column.

4.3.2 Analytical Column - C_{18} reversed-phase column, 100 mm x 2 mm ID, 5-µm particle size of ODS-Hypersil; or C_8 reversed phase column, 100 mm x 2 mm ID, 3-µm particle size of MOS2-Hypersil, or equivalent.

4.4 Purification equipment for azo dye standards

4.4.1 Soxhlet extraction apparatus

4.4.2 Extraction thimbles - single thickness, 43 x 123 mm

4.4.3 Filter paper, 9.0 cm (Whatman qualitative No. 1 or equivalent).

4.4.4 Silica-gel column - 3 in. x 8 in., packed with silica gel (Type 60, EM reagent 70/230 mesh).

4.5 Extraction equipment for chlorinated phenoxyacid compounds

4.5.1 Erlenmeyer flasks - 500-mL wide-mouth glass, 500-mL glass, with 24/40 ground-glass joint, 1000-mL glass.

4.5.2 Separatory funnel - 2000-mL.

4.5.3 Graduated cylinder - 1000-mL.

4.5.4 Funnel - 75-mm diameter.

4.5.5 Wrist shaker - Burrell Model 75 or equivalent.

4.5.6 pH meter.

4.6 Kuderna-Danish (K-D) apparatus (optional).

4.6.1 Concentrator tube - 10-mL graduated. A ground-glass stopper is used to prevent evaporation of extracts.

4.6.2 Evaporation flask - 500-mL. Attach to concentrator tube with springs, clamps, or equivalent.

4.6.3 Two-ball micro-Snyder column

4.6.4 Springs - ½ in.

4.6.5 Solvent vapor recovery system (Kontes K-545000-1006 or K-547300-0000, Ace Glass 6614-30, or equivalent).

NOTE: This glassware is recommended for the purpose of solvent recovery during the concentration procedures requiring the use of Kuderna-Danish evaporative concentrators. Incorporation of this apparatus may be required by State or local municipality regulations that govern air emissions of volatile organics. EPA recommends the incorporation of this type of reclamation system as a method to implement an emissions reduction program. Solvent recovery is a means to conform with waste minimization and pollution prevention initiatives.

4.7 Disposable serological pipets

4.8 Collection tube - 15-mL conical, graduated.

4.9 Vials - 5-mL conical, glass, with PTFE-lined screw-caps or crimp tops.

4.10 Glass wool

4.11 Microsyringes - 100-µL, 50-µL, 10-µL (Hamilton 701 N or equivalent), and 50 µL (Blunted, Hamilton 705SNR or equivalent).

4.12 Rotary evaporator - Equipped with 1000-mL receiving flask.

4.13 Balances - Analytical, 0.0001 g, top-loading, 0.01 g.

4.14 Volumetric flasks, Class A - 10-mL to 1000-mL.

4.15 Graduated cylinder - 100-mL.

4.16 Separatory funnel - 250-mL.

4.17 Separatory funnel - 2-L, with PTFE stopcock.

4.18 Concentrator adaptor (optional) - for carbamate extraction.

4.19 Nitrogen evaporation apparatus - N-Evap Analytical Evaporator Model 111, Organomation Association Inc., Northborough, MA, or equivalent.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Organic-free reagent water. All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

5.3 Sodium sulfate (granular, anhydrous), Na_2SO_4. Purify by heating at 400°C for 4 hours in a shallow tray, or by precleaning the sodium sulfate with methylene chloride.

5.4 Ammonium acetate, NH_4OOCCH_3, solution (0.1 M). Filter through a 0.45-µm membrane filter (Millipore HA or equivalent).

5.5 Acetic acid, CH_3CO_2H

5.6 Sulfuric acid solution

5.6.1 (1:1, v/v) - Slowly add 50 mL H_2SO_4 (sp. gr. 1.84) to 50 mL of water.

5.6.2 (1:3, v/v) - Slowly add 25 mL H_2SO_4 (sp. gr. 1.84) to 75 mL of water.

5.7 Argon gas, 99+% pure.

5.8 Solvents - Unless otherwise noted, all solvents must be pesticide quality or equivalent.

5.8.1 Methylene chloride, CH_2Cl_2

5.8.2 Toluene, $C_6H_5CH_3$

5.8.3 Acetone, CH_3COCH_3

5.8.4 Diethyl Ether, $C_2H_5OC_2H_5$ - Must be free of peroxides as indicated by test strips (EM Quant, or equivalent). Procedures for removal of peroxides are provided with the test strips. After cleanup, 20 mL of ethyl alcohol preservative must be added to each liter of ether.

5.8.5 Methanol, CH_3OH - HPLC quality or equivalent.

5.8.6 Acetonitrile, CH_3CN - HPLC quality or equivalent.

5.8.7 Ethyl acetate, $CH_3CO_2C_2H_5$

5.9 Standard materials - pure standard materials or certified solutions of each analyte targeted for analysis. Disperse azo dyes must be purified before use according to Sec. 5.10.

WARNING: Tris-BP has been classified as a carcinogen. Purified standard material and stock standard solutions should be handled in a hood.

5.10 Disperse azo dye purification

Two procedures are involved. The first step is the Soxhlet extraction of the dye for 24 hours with toluene and evaporation of the liquid extract to dryness, using a rotary evaporator. The solid is then recrystallized from toluene, and dried in an oven at approximately 100°C. If this step does not give the required purity, column chromatography should be employed. Load the solid onto a 3 x 8 inch silica gel column (Sec. 4.4.4), and elute with diethyl ether. Separate impurities chromatographically, and collect the major dye fraction.

5.11 Stock standard solutions - Standards may be prepared from pure standard materials or may be purchased as certified solutions. Commercially-prepared stock standards may be used if they are certified by the manufacturer and verified against a standard made from pure material.

5.11.1 Prepare stock standard solutions by accurately weighing 0.0100 g of pure material. Dissolve the material in methanol or other suitable solvent (e.g., prepare Tris-BP in ethyl acetate), and dilute to known volume in a volumetric flask.

NOTE: Due to the reactivity of the chlorinated herbicides, the standards must be prepared in acetonitrile. Methylation will occur if standards are prepared in methanol.

If compound purity is certified at 96% or greater, the weight can be used without correction to calculate the concentration of the stock standard. Commercially-prepared stock standards can be used at any concentration if they are certified by the manufacturer or by an independent source.

5.11.2 Transfer the stock standard solutions into glass vials with PTFE-lined screw-caps or crimp-tops. Store at 4°C and protect from light. Stock standard solutions should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards.

5.12 Calibration standards - A minimum of five different concentrations for each parameter of interest should be prepared through dilution of the stock standards with methanol (or other suitable solvent). At least one of the calibration standards should correspond to a sample concentration at or below that necessary to meet the data quality objectives of the project. The remaining concentrations should correspond to the expected range of concentrations found in real samples, or should define the working range of the HPLC-UV or HPLC-TS/MS system (see Method 8000). Calibration standards must be replaced after one or two months, or sooner if comparison with check standards indicates a problem.

5.13 Surrogate standards - The analyst should monitor the performance of the extraction, cleanup (when used), and analytical system, along with the effectiveness of the method in dealing with each sample matrix, by spiking each sample, standard, and blank with one or two surrogates (e.g., organophosphorus or chlorinated phenoxyacid compounds not expected to be present in the sample).

5.14 HPLC/MS tuning standard - Polyethylene glycol 400 (PEG-400), PEG-600, or PEG-800 are recommended as tuning standards. However, analysts may use other tuning standards as recommended by the instrument manufacturer or other documented source. If one of the PEG solutions is used, dilute to 10 percent (v/v) in methanol. Which PEG is used will depend upon analyte molecular weight range: m.w. <500, use PEG-400; m.w. >500, use PEG-600 or PEG-800.

5.15 Internal standards - When the internal standard calibration option is used for HPLC/MS analyses, it is recommended that analysts use stable isotopically-labeled compounds of the same chemical class when they are available (e.g., $^{13}C_6$-carbofuran may be used as an internal standard in the analysis of carbamates).

5.16 Matrix spiking standards - Consult Method 3500 for information on matrix spiking solutions. Prepare a solution containing the analytes of interest in a suitable solvent.

NOTE: The form of the compounds used for spiking should be identical to the form of the target analytes. For the phenoxyacid herbicides in particular, use the acid form of the acid analytes, not the ester form or an ether, as use of these other forms will not represent the performance of the overall extraction, cleanup, and determinative methods relative to the target analytes. Conversely, when the ester forms are of the analytes of interest, e.g.,

2,4-D, butoxyethanol ester, use the ester form of the analyte for preparing matrix spiking solutions.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

See the introductory material to Chapter Four, Organic Analytes, Sec. 4.1.

7.0 PROCEDURE

7.1 Sample preparation

Prior to analysis, samples must be extracted using either an appropriate 3500 series method or using specific procedures described in this method.

7.1.1 Samples for analysis of disperse azo dyes and organophosphorus compounds must be prepared by an appropriate 3500 series method prior to HPLC/MS analysis.

7.1.2 Samples for the analysis of Tris(2,3-dibromopropyl)phosphate (Tris-BP) must be prepared according to Sec. 7.2, prior to HPLC/MS analysis.

7.1.3 Samples for the analysis of chlorinated phenoxyacid compounds and their esters should be prepared according to Sec. 7.3, or other appropriate technique, prior to HPLC/MS analysis. TCLP leachates to be analyzed for the phenoxyacid herbicides may also be prepared using solid-phase extraction (SPE), as described in Method 3535.

7.2 Microextraction of Tris-BP

7.2.1 Solid samples

7.2.1.1 Weigh a 1-g portion of the sample into a tared beaker. If the sample appears moist, add an equivalent amount of anhydrous sodium sulfate and mix well. Add 100 µL of Tris-BP (approximate concentration 1000 mg/L) to the sample selected for spiking; the amount added should result in a final concentration of 100 ng/µL in the 1-mL extract.

7.2.1.2 Remove the glass wool plug from a disposable serological pipet. Insert a 1 cm plug of clean silane treated glass wool to the bottom (narrow end) of the pipet. Pack 2 cm of anhydrous sodium sulfate onto the top of the glass wool. Wash pipet and contents with 3 - 5 mL of methanol.

7.2.1.3 Pack the sample into the pipet prepared according to Sec. 7.2.1.2. If packing material has dried, wet with a few mL of methanol first, then pack sample into the pipet.

7.2.1.4 Extract the sample with 3 mL of methanol followed by 4 mL of 50% (v/v) methanol/methylene chloride (rinse the sample beaker with each volume of extraction solvent prior to adding it to the pipet containing the sample). Collect the extract in a 15-mL graduated glass tube.

7.2.1.5 Evaporate the extract to 1 mL using the nitrogen evaporation technique (Sec. 7.5). Record the volume. It may not be possible to evaporate some sludge samples to a reasonable concentration.

7.2.1.6 Determination of percent dry weight - When sample results are to be calculated on a dry weight basis, a second portion of sample should be weighed at the same time as the portion used for analytical determination.

WARNING: The drying oven should be contained in a hood or be vented. Significant laboratory contamination may result from drying a heavily contaminated sample.

Immediately after weighing the sample for extraction, weigh 5 - 10 g of the sample into a tared crucible. Dry this aliquot overnight at 105°C. Allow to cool in a desiccator before weighing. Calculate the % dry weight as follows:

$$\%\ \text{dry weight} = \frac{\text{g of dry sample}}{\text{g of sample}} \times 100$$

This oven-dried aliquot is not used for the extraction and should be disposed of appropriately once the dry weight has been determined.

7.2.2 Aqueous samples

7.2.2.1 Using a 100-mL graduated cylinder, measure 100 mL of sample and transfer it to a 250-mL separatory funnel. Add 200 µL of Tris-BP (approximate concentration 1000 mg/L) to the sample selected for spiking; the amount added should result in a final concentration of 200 ng/µL in the 1-mL extract.

7.2.2.2 Add 10 mL of methylene chloride to the separatory funnel. Seal and shake the separatory funnel three times, approximately 30 seconds each time, with periodic venting to release excess pressure.

NOTE: Methylene chloride creates excessive pressure rapidly; therefore, initial venting should be done immediately after the separatory funnel has been sealed and shaken once. Methylene chloride is a suspected carcinogen, use necessary safety precautions.

7.2.2.3 Allow the organic layer to separate from the water phase for a minimum of 10 minutes. If the emulsion interface between layers is more than one-third the size of the solvent layer, the analyst must employ mechanical techniques to complete phase separation. See Section 7 of Method 3510.

7.2.2.4 Collect the extract in a 15-mL graduated glass tube. Concentrate the extract to 1 mL, using nitrogen evaporation (Sec. 7.5).

7.3 Extraction for chlorinated phenoxyacid compounds

Preparation of soil, sediment, and other solid samples should follow the procedures outlined in Method 8151, or other appropriate technique, with the exception of no hydrolysis or esterification is generally performed. However, if the analyst desires to determine all of the phenoxyacid moieties

as the acid, hydrolysis may be performed. Sec. 7.3.1 presents an outline of the procedure with the appropriate changes necessary for determination by Method 8321. Sec. 7.3.2 describes the extraction procedure for aqueous samples. TCLP leachates may be extracted using solid-phase extraction, as described in Method 3535.

7.3.1 Extraction of solid samples

7.3.1.1 Add 50 g of soil/sediment sample to a 500-mL, wide-mouth Erlenmeyer flask. Add spiking solutions, if required, mix well and allow to stand for 15 minutes. Add 50 mL of organic-free reagent water and stir for 30 minutes. Determine the pH of the sample with a glass electrode and pH meter, while stirring. Adjust the pH to 2 with cold H_2SO_4 (1:1) and monitor the pH for 15 minutes, with stirring. If necessary, add additional H_2SO_4 until the pH remains at 2.

7.3.1.2 Add 20 mL of acetone to the flask, and mix the contents with the wrist shaker for 20 minutes. Add 80 mL of diethyl ether to the same flask, and shake again for 20 minutes. Decant the extract and measure the volume of solvent recovered.

7.3.1.3 Extract the sample twice more using 20 mL of acetone followed by 80 mL of diethyl ether. After addition of each solvent, the mixture should be shaken with the wrist shaker for 10 minutes and the acetone-ether extract decanted.

7.3.1.4 After the third extraction, the volume of extract recovered should be at least 75% of the volume of added solvent. If this is not the case, additional extractions may be necessary. Combine the extracts in a 2000-mL separatory funnel containing 250 mL of 5% acidified sodium sulfate. If an emulsion forms, slowly add 5 g of acidified sodium sulfate (anhydrous) until the solvent-water mixture separates. A quantity of acidified sodium sulfate equal to the weight of the sample may be added, if necessary.

7.3.1.5 Check the pH of the extract. If it is not at or below pH 2, add more concentrated H_2SO_4 until the extract is stabilized at the desired pH. Gently mix the contents of the separatory funnel for 1 minute and allow the layers to separate. Collect the aqueous phase in a clean beaker, and the extract phase (top layer) in a 500-mL Erlenmeyer flask with a ground-glass stopper. Place the aqueous phase back into the separatory funnel and re-extract using 25 mL of diethyl ether. Allow the layers to separate and discard the aqueous layer. Combine the ether extracts in the 500-mL Erlenmeyer flask.

7.3.1.6 Add 45 - 50 g acidified anhydrous sodium sulfate to the combined ether extracts. Allow the extract to remain in contact with the sodium sulfate for approximately 2 hours.

NOTE: The drying step is very critical. Any moisture remaining in the ether will result in low recoveries. The amount of sodium sulfate used is adequate if some free flowing crystals are visible when swirling the flask. If all of the sodium sulfate solidifies in a cake, add a few additional grams of acidified sodium sulfate and again test by swirling. The 2-hour drying time is a minimum; however, the extracts may be held overnight in contact with the sodium sulfate.

7.3.1.7 Transfer the ether extract, through a funnel plugged with acid-washed glass wool, into a 500-mL K-D flask equipped with a 10-mL concentrator tube. Use a glass rod to crush caked sodium sulfate during the transfer. Rinse the Erlenmeyer flask and column with 20-30 mL of diethyl ether to complete the quantitative transfer. Reduce the volume of the extract using the macro K-D technique (Sec. 7.5).

7.3.2 Extraction of aqueous samples

7.3.2.1 Using a 1000-mL graduated cylinder, measure 1 liter (nominal) of sample, record the sample volume to the nearest 5 mL, and transfer it to a separatory funnel. If high concentrations are anticipated, a smaller volume may be used and then diluted with organic-free reagent water to 1 liter. Adjust the pH to less than 2 with sulfuric acid (1:1).

7.3.2.2 Add 150 mL of diethyl ether to the sample bottle, seal, and shake for 30 seconds to rinse the walls. Transfer the solvent wash to the separatory funnel and extract the sample by shaking the funnel for 2 minutes with periodic venting to release excess pressure. Allow the organic layer to separate from the water layer for a minimum of 10 minutes. If the emulsion interface between layers is more than one-third the size of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample, and may include stirring, filtration of the emulsion through glass wool, centrifugation, or other physical methods. Drain the aqueous phase into a 1000-mL Erlenmeyer flask.

7.3.2.3 Repeat the extraction two more times using 100 mL of diethyl ether each time. Combine the extracts in a 500-mL Erlenmeyer flask. (Rinse the 1000-mL flask with each additional aliquot of extracting solvent to make a quantitative transfer.)

7.3.2.4 Proceed to Sec. 7.5 for drying, K-D concentration, solvent exchange, and final volume adjustment.

7.4 Extraction of carbamates

Preparation of aqueous , soil, sediment, and other solid samples must follow an appropriate 3500 series method. The following sections provide general considerations.

7.4.1 One-liter aqueous samples are extracted with methylene chloride using an appropriate 3500 series method.

7.4.2 Forty-gram quantities of solid samples are extracted with methylene chloride using an appropriate 3500 series method.

7.4.3 Concentration steps can be performed using a rotary evaporator or K-D, reducing the final extract to 5-10 mL.

7.4.4 Final concentration of the extract and exchanging the solvent to a 1-mL final volume of methanol may be accomplished using an adaptor on the rotary evaporator. If an

adaptor is unavailable, the final concentration may be performed using nitrogen evaporation, in a fume hood.

7.5 Extract concentration techniques

Two procedures are provided for the concentration of extracts: macro-concentration by Kuderna-Danish (K-D) and micro-concentration by nitrogen evaporation.

7.5.1 Macro-concentration by K-D

Add one or two clean boiling chips to the flask and attach a three-ball macro-Snyder column. Attach the solvent vapor recovery glassware (condenser and collection device, Sec. 4.6.5) to the Snyder column of the K-D apparatus following manufacturer's instructions. Prewet the Snyder column by adding about 1 mL of diethyl ether to the top. Place the apparatus on a hot water bath (60°-65°C) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed in vapor. Adjust the vertical position of the apparatus and the water temperature, as required, to complete the concentration in 15-20 minutes. At the proper rate of distillation the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 5 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 minutes.

7.5.2 Solvent exchange

Prior to analysis, the final extract solvent must be exchanged to methanol or acetonitrile.

7.5.2.1 Transfer the concentrator tube to a nitrogen evaporation device. Add a total of 5 mL of the final solvent of choice (methanol or acetonitrile).

7.5.2.2 Reduce the extract volume according to Sec. 7.5.3 and adjust the final volume to 1 mL (or other volume necessary to achieve the required sensitivity).

7.5.3 Micro-concentration by nitrogen evaporation

7.5.3.1 Place the concentrator tube in a warm water bath (approximately 35°C) and evaporate the solvent volume to the required level using a gentle stream of clean, dry nitrogen (filtered through a column of activated carbon).

CAUTION: Do not use plasticized tubing between the carbon trap and the sample.

7.5.3.2 The internal wall of the tube must be rinsed down several times with the final solvent during the operation. During evaporation, the solvent level in the tube must be positioned to prevent water from condensing into the sample (i.e., the solvent level should be below the level of the water bath). Under normal operating conditions, the extract should not be allowed to become dry.

7.5.4 Transfer the extract to a glass vial with a PTFE-lined screw-cap or crimp-top and store refrigerated at 4°C. Proceed with HPLC analysis.

7.6 HPLC chromatographic conditions

7.6.1 Recommended mobile phases and elution gradients for some groups of analytes are shown in Tables 1 and 2. Analysts should also consult the instrument manufacturer's instructions. In the absence of specific recommendations, the following conditions may be a useful starting point.

Flow rate	0.8 mL/min
Post-column mobile phase	0.1 M ammonium acetate (1% methanol)/(0.1 M ammonium acetate for phenoxyacid compounds)
Post-column flow rate	0.4 mL/min

Optimize the instrumental conditions for resolution of the target analytes and sensitivity. Post-column addition of the MS ionization reagents may not be necessary in all instances, and these reagents may be added to the elution solvents, provided that adequate performance can be demonstrated.

NOTE: Once established, the same operating conditions must be used for both calibrations and sample analyses.

7.6.2 If there is a chromatographic problem from compound retention when analyzing disperse azo dyes, organophosphorus compounds, or tris(2,3-dibromo-propyl)phosphate, a 2% constant flow of methylene chloride may be applied as needed. Methylene chloride/aqueous methanol solutions must be used with caution as HPLC eluants. Acetic acid (1%), another mobile phase modifier, can be used with compounds with acid functional groups.

7.6.3 A total flow rate of 1.0 to 1.5 mL/min may be necessary to maintain thermospray ionization, however, consult the instrument manufacturer's instructions and adjust the flow rate as needed.

7.7 Recommended thermospray/MS operating conditions

Prior to analysis of samples, the analyst should evaluate the relative sensitivity of the target compounds to each ionization mode to determine which may provide better sensitivity during analyses. This evaluation may be based on the structures of the analytes or by conducting analyses in each of the two ionization modes. Some groups of target compounds will have much better sensitivity using either positive or negative ionization (e.g., carbamates are generally more sensitive to the positive ionization mode and phenoxyacids are generally more sensitive to the negative ionization mode). When all the analytes of interest for a given application respond adequately in a given ionization mode, a single analysis using that mode may be employed.

7.7.1 Positive ionization mode conditions

Discharge electrode	Off
Filament	On or off (optional, analyte dependent)
Mass range	150 to 450 amu (analyte dependent, expect 1 to 18 amu higher than molecular weight of the compound).
Scan time	1.50 sec/scan

Optional repeller wire or plate	170 to 250 v (sensitivity optimized). See Figure 2 for schematic of source with wire repeller.

7.7.2 Negative ionization mode conditions

Discharge electrode	On
Filament	Off
Mass Range	135 to 450 amu
Scan time	1.50 sec/scan

7.7.3 Thermospray temperatures

Vaporizer control	110 to 130°C
Vaporizer tip	200 to 215°C
Jet	210 to 220°C
Source block	230 to 265°C. (Some compounds may degrade in the source block at higher temperatures, operator should use knowledge of chemical properties to estimate proper source temperature).

7.7.4 Sample injection volume

An injection volume of 20 to 100 µL is normally used. The injection loop must be overfilled by, minimally, a factor of two (e.g., 20-µL sample used to overfill a 10-µL injection loop) when manual injections are performed. If solids are present in the extract, allow them to settle or centrifuge the extract and withdraw the injection volume from the clear layer.

7.8 Calibration

7.8.1 Thermospray/MS system

When an MS detector is employed, the system must be tuned on quadrupole 1 (and quadrupole 3 for triple quadrupoles) for accurate mass assignment, sensitivity, and resolution. It is recommended that this be accomplished using polyethylene glycol (PEG) 400, 600, or 800 (see Sec. 5.14) which have average molecular weights of 400, 600, and 800, respectively. Analysts may use other tuning standards as recommended by the instrument manufacturer or other documented source. If PEGs are used, a mixture of these PEGs can be made such that it will approximate the expected working mass range for the analyses. Use PEG 400 for analysis of chlorinated phenoxyacid compounds. The PEG is introduced via the thermospray interface, circumventing the HPLC.

7.8.1.1 The mass calibration parameters are as follows:

PEG 400 and 600		PEG 800	
Mass range	15 to 765 amu	Mass range	15 to 900 amu
Scan time	0.5 to 5.0 sec/scan	Scan time	0.5 to 5.0 sec/scan

Approximately 100 scans should be acquired, with 2 to 3 injections made. The scan with the best fit to the accurate mass table (see Tables 7 and 8) should be used as the calibration table. If calibrants other than PEG are used, the mass range should be from 15 to approximately 20 amu higher than the highest mass used for calibration. A scan time should be chosen which will give at least 6 scans across the calibrant peak.

7.8.1.2 The low mass range from 15 to 100 amu is covered by the ions from the ammonium acetate buffer used in the thermospray process.

NH_4^+	18 amu
$NH_4^+ \cdot H_20$	36 amu
$CH_3OH \cdot NH_4^+$	50 amu (methanol)
$CH_3 CN \cdot NH_4^+$	59 amu (acetonitrile)
$CH_3 OOH \cdot NH_4^+$	78 amu (acetic acid)

The appearance of m/z 50 or 59 depends upon the use of methanol or acetonitrile as the organic modifier. The higher mass range is covered by the ammonium ion adducts of the various ethylene glycols (e.g., $H(OCH_2CH_2)_nOH$ where n=4, gives the $H(OCH_2CH_2)_4OH \bullet NH_4^+$ ion at m/z 212).

7.8.2 Liquid chromatographic system

7.8.2.1 Choose the proper ionization conditions for the MS detector, as outlined in Sec. 7.7. When UV detection is employed in conjunction with the MS detector, establish appropriate operating conditions for the UV detector.

7.8.2.2 Prepare five calibration standards (see Sec. 5.12 and Method 8000). Inject each calibration standard onto the HPLC, using the chromatographic conditions outlined in Table 1. Refer to Sec. 7.0 of Method 8000 for guidance on external and internal calibration options and calibration acceptance criteria. In most cases the $(M^+H)^+$ and $(M^+NH_4)^+$ adduct ions are the only ions of significant abundance. For example, Table 9 lists the retention times and the major ions (>5%) present in the positive ionization thermospray single quadrupole spectra of the organophosphorus compounds.

7.8.2.3 The use of selective ion monitoring (SIM) is acceptable in situations requiring detection limits below the normal range of full spectra analysis. However, SIM may provide a lesser degree of confidence in the compound identification unless multiple ions are monitored for each compound.

7.8.2.4 The use of selective reaction monitoring (SRM) is also acceptable when using triple-quad MS/MS and enhanced sensitivity is needed.

7.8.2.5 If UV detection is being used, integrate the area under the full chromatographic peak for each concentration. Quantitation by HPLC-UV may be preferred if it is known that sample interference and/or analyte coelution are not a

problem, or when response of the MS detector is not sufficiently stable for quantitative analyses. In these instances, the MS response may be used for positive qualitative identification of the analytes while the UV response is used for quantitation.

7.8.2.6 The retention time of the chromatographic peak is an important variable in analyte identification. Therefore, the relative retention time of the analyte (versus the internal standard) should be in the range of 0.9 to 1.1.

7.8.3 Calibration verification

At the beginning of each analytical shift, the response of the instrument system must be verified by the analysis of a single standard at the approximate mid-point of the initial calibration range. Consult Method 8000 for information on performing this demonstration and the acceptance criteria that should be employed.

7.9 Sample Analysis

Once the LC system has been calibrated as outlined in Sec. 7.8, it is ready for sample analysis, employing both MS and UV detectors. Depending on the sensitivity necessary for a given project, analyses may be conducted using the MS detector in either the positive or negative ionization modes. The positive ionization mode generally provides greater sensitivity, and may be more appropriate for samples containing very low concentrations of the analytes of interest. However, analyst are advised that some compounds may be detectable in only the negative ionization mode.

7.9.1 An instrument blank (methanol) should be analyzed after the standards, in order to demonstrate that the system is free from contamination.

7.9.2 If performing manual injections, take an appropriate aliquot of the sample as per Sec. 7.7.4. Start the HPLC gradient elution, load and inject the sample aliquot, and start the mass spectrometer data system analysis.

7.9.3 If using an autoinjector, ensure that it is set up properly according to the manufacturer's instructions and that all samples and standards are loaded in the proper order. Start the autoinjector, the HPLC gradient elution, and the mass spectrometer data system.

7.9.4 The concentration of the analyte is determined by using the initial calibration data (see Method 8000) from either the MS or UV detector response. Samples whose concentrations exceed the calibration range must be diluted to fall within the range.

7.9.5 When using MS or MS/MS, and when it is appropriate for the compounds of interest and the project objectives, determinations in both positive and negative ionization analyses may be done on each sample extract.

7.10 Calculations

7.10.1 Using the external or internal standard calibration procedure (Method 8000), determine the identity and quantity of each component peak in the sample reconstructed ion chromatogram which corresponds to the compounds used for calibration processes. See Method 8000 for calculations.

7.10.2 The retention time of the chromatographic peak is an important parameter for the identity of the analyte. However, because matrix interferences can change chromatographic column conditions, the absolute retention times are not as significant as relative retention times (when using internal standards), and the mass spectral patterns are important criteria for analyte identification.

7.10.3 In instances when the TS/MS response exhibits higher variability, the MS response may be used to identify the analytes of interest while the quantitative results are derived from the response of the UV detector.

7.11 Optional MS/MS confirmation

With respect to this method, MS/MS shall be defined as the daughter ion collision activated dissociation acquisition with quadrupole one set on one mass (parent ion), quadrupole two pressurized with argon and with a higher offset voltage than normal, and quadrupole three set to scan desired mass range.

7.11.1 Since the thermospray process often generates only one or two ions per compound, the use of MS/MS is a more specific mode of operation yielding molecular structural information. In this mode, samples can be rapidly screened through direct injection of the sample into the thermospray (e.g., without using the HPLC to separate the sample components).

7.11.2 When using MS/MS, the first quadrupole should be set to the protonated molecule or ammoniated adduct of the analyte of interest. The third quadrupole should be set to scan from 30 amu to just above the mass region of the protonated molecule.

7.11.3 The collision gas pressure (Ar) should be set at about 1.0 mTorr and the collision energy at 20 eV. If these parameters fail to give considerable fragmentation, the settings may be increased to create more and stronger collisions.

7.11.4 For analytical determinations, the base peak of the collision spectrum shall be taken as the quantitation ion. For extra specificity, a second ion should be chosen as a backup quantitation ion.

7.11.5 Perform an initial calibration, as outlined in Sec. 7.8.

7.11.6 MS/MS contamination and interferences

7.11.6.1 If the MS/MS mode is to be used without chromatographic separation (rapid screening), then the method blank analysis must show that the sample preparation and analysis procedures are free of contamination by the analyte of interest or by interfering compounds. Refer to Sec. 8.0 of Method 8000 for guidance on acceptable method blank performance. If contamination is detected in the method blank above acceptable limits, re-extraction and reanalysis of the affected samples is necessary.

7.11.6.2 The MS/MS spectra of a calibration standard and the sample should be compared and the ratios of the three major (most intense) ions examined. These ratios should be approximately the same unless there is an interference. If an interference appears, chromatographic separation must be utilized.

7.11.6.3 The signal of the target analyte in a sample may be suppressed by co-extracted interferences which do not give a signal in the monitored ions. In order to monitor such signal suppression, an internal standard may be spiked into all standards, blanks, and sample extracts at a consistent concentration prior to analysis. The internal standard may be any compound which responds well in the appropriate ionization mode and which is not likely to be found in nature. (Note: Atrazine-d_5 has been used successfully for positive ion analysis, while 2,6-dinitrotoluene-d_3 has been used successfully for negative ion analysis.) The amount spiked should be chosen such that the signal produced is at least 100 times the noise level for the appropriate ion. The signal of the internal standard should be monitored. Reanalysis is required for any sample in which the internal standard peak height varies by more than 30% from the average internal standard height obtained during the five-point calibration. If reanalysis confirms this variance in signal, the sample should be reanalyzed using a chromatographic separation. Quantitation of analyte concentration may be performed using this internal standard. External standard quantitation is also allowed.

7.11.7 The total area of the quantitation ion(s) is calculated and the initial calibration is used to calculate sample results.

7.11.8 MS/MS techniques can also be used to perform structural analysis on ions represented by unassigned m/z ratios. The procedure for compounds of unknown structures is to set up a CAD experiment on the ion of interest. The spectrum generated from this experiment will reflect the structure of the compound by its fragmentation pattern. A trained mass spectroscopist and some history of the sample are usually needed to interpret the spectrum. (CAD experiments on actual standards of the expected compound are necessary for confirmation or denial of that substance.)

7.12 Optional wire-repeller CAD confirmation

7.12.1 See Figure 3 for the correct position of the wire-repeller in the thermospray source block.

7.12.2 Once the wire-repeller is inserted into the thermospray flow, the voltage can be increased to approximately 500 - 700 v. Enough voltage is necessary to create fragment ions, but not so much that shorting occurs.

7.12.3 Continue as outlined in Sec. 7.9.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One and Method 8000 for specific quality control (QC) procedures. Each laboratory should maintain a formal quality assurance program. The laboratory should also maintain records to document the quality of the data generated.

8.2 Quality control procedures necessary to evaluate the HPLC system operation are found in Method 8000 and include evaluation of retention time windows, calibration verification and chromatographic analysis of samples. Check the performance of the entire analytical system daily

using data gathered from analyses of blanks, standards, and replicate samples. If any of the chromatographic QC limits are not met, the analyst should examine the LC system for:

- Leaks,
- Proper pressure delivery,
- A dirty guard column; may need replacing or repacking, and
- Possible partial thermospray plugging.

Checking any of the above items will necessitate shutting down the HPLC/TS system, making repairs and/or replacements, and then restarting the analyses. A calibration verification standard should be reanalyzed before any sample analyses, as described in Sec. 7.8.3.

8.3 Initial demonstration of proficiency - Each laboratory must demonstrate initial proficiency with each sample preparation and determinative method combination it utilizes, by generating data of acceptable accuracy and precision for target analytes in a clean matrix. The laboratory must also repeat the following operations whenever new staff are trained or significant changes in instrumentation are made. See Method 8000, Sec. 8.0 for information on how to accomplish this demonstration.

8.4 Sample quality control for preparation and analysis - The laboratory must also have procedures for documenting the effect of the matrix on method performance (precision, accuracy, and detection limit). At a minimum, this includes the analysis of QC samples including a method blank, matrix spike, a duplicate, and a laboratory control sample (LCS) in each analytical batch and the addition of surrogates to each field sample and QC sample.

8.4.1 Documenting the effect of the matrix should include the analysis of at least one matrix spike and one duplicate unspiked sample or one matrix spike/matrix spike duplicate pair. The decision on whether to prepare and analyze duplicate samples or a matrix spike/matrix spike duplicate must be based on a knowledge of the samples in the sample batch. If samples are expected to contain target analytes, then laboratories may use one matrix spike and a duplicate analysis of an unspiked field sample. If samples are not expected to contain target analytes, laboratories should use a matrix spike and matrix spike duplicate pair.

8.4.2 A laboratory control sample (LCS) should be included with each analytical batch. The LCS consists of an aliquot of a clean (control) matrix similar to the sample matrix and of the same weight or volume. The LCS is spiked with the same analytes at the same concentrations as the matrix spike. When the results of the matrix spike analysis indicate a potential problem due to the sample matrix itself, the LCS results are used to verify that the laboratory can perform the analysis in a clean matrix.

8.4.3 See Method 8000, Sec. 8.0 for the details on carrying out sample quality control procedures for preparation and analysis.

8.5 Surrogate recoveries - The laboratory must evaluate surrogate recovery data from individual samples versus the surrogate control limits developed by the laboratory. See Method 8000, Sec. 8.0 for information on evaluating surrogate data and developing and updating surrogate limits.

8.6 It is recommended that the laboratory adopt additional quality assurance practices for use with this method. The specific practices that are most productive depend upon the needs of

the laboratory and the nature of the samples. Whenever possible, the laboratory should analyze standard reference materials and participate in relevant performance evaluation studies.

9.0 METHOD PERFORMANCE

9.1 Single operator accuracy and precision studies have been conducted using spiked sediment, wastewater, sludge, and water samples. Tables 4, 5, and 6 provide single-laboratory data for Disperse Red 1. Table 1 provides the data for organophosphorus pesticides, Table 11 for Tris-BP, Table 12 for chlorophenoxyacid herbicides, and Tables 14 and 15 for carbamates.

9.2 Table 13 presents multi-laboratory accuracy and precision data for the chlorinated phenoxyacid herbicides. The data summary is based on data from three laboratories that analyzed duplicate solvent solutions at each concentration specified in the table.

9.3 Tables 16 and 17 present the multi-laboratory accuracy and precision data for the carbamates. The data summary is based on data from nine laboratories that analyzed triplicate solvent solutions at each concentration level specified in the tables.

9.4 Table 18 provides data for solid-phase extraction of 2,4-D and 2,4,5-TP spiked into TCLP buffers at two different spiking levels.

10.0 REFERENCES

1. Voyksner, R.D., Haney, C.A., "Optimization and Application of Thermospray High-Performance Liquid Chromatography/Mass Spectrometry", Anal. Chem., 1985, 57, 991-996.

2. Blakley, C.R., Vestal, M.L., "Thermospray Interface for Liquid Chromatography/Mass Spectrometry", Anal. Chem., 1983, 55, 750-754.

3. Taylor, V., Hickey, D.M., Marsden, P.J., "Single Laboratory Validation of EPA Method 8140", EPA-600/4-87/009, U.S. Environmental Protection Agency, Las Vegas, NV, 1987, 144 pp.

4. "Guidelines for Data Acquisition and Data Quality Evaluation in Environmental Chemistry", Anal. Chem., 1980, 52, 2242-2249.

5. Betowski, L.D., Jones, T.L., "The Analysis of Organophosphorus Pesticide Samples by HPLC/MS and HPLC/MS/MS", Environmental Science and Technology, 1988.

8. U.S. EPA: 2nd Annual Report on Carcinogens, NTP 81-43, Dec. 1981, pp. 236-237.

9. Blum, A., Ames, B.N., Science 195, 1977, 17.

10. Zweidinger, R.A., Cooper, S.D., Pellazari, E.D., Measurements of Organic Pollutants in Water and Wastewater, ASTM 686.

11. Cremlyn, R., Pesticides: Preparation and mode of Action, John Wiley and Sons, Chichester, 1978, p. 142.

12. Cotterill, E.G., Byast, T.H., "HPLC of Pesticide Residues in Environmental Samples", In Liquid Chromatography in Environmental Analysis, Laurence, J.F., Ed., Humana Press, Clifton, NJ, 1984.

13. Voyksner, R.D., "Thermospray HPLC/MS for Monitoring the Environment", In Applications of New Mass Spectrometry Techniques in Pesticide Chemistry; Rosen, J.D., Ed., John Wiley and Sons: New York, 1987.

14. Yinon, J., Jones, T.L., Betowski, L.D., Rap. Comm. Mass Spectrom., 1989, 3, 38.

15. Shore, F.L., Amick, E.N., Pan, S.T., Gurka, D.F., "Single Laboratory Validation of EPA Method 8150 for the Analysis of Chlorinated Herbicides in Hazardous Waste", EPA/600/4-85/060, U.S. Environmental Protection Agency, Las Vegas, NV, 1985.

16. "Development and Evaluations of an LC/MS/MS Protocol", EPA/600/X-86/328, Dec. 1986.

17. "An LC/MS Performance Evaluation Study of Organophosphorus Pesticides", EPA/600/X-89/006, Jan. 1989.

18. "A Performance Evaluation Study of a Liquid Chromatography/Mass Spectrometry Method for Tris-(2,3-Dibromopropyl) Phosphate", EPA/600/X-89/135, June 1989.

19. "Liquid Chromatography/Mass Spectrometry Performance Evaluation of Chlorinated Phenoxyacid Herbicides and Their Esters", EPA/600/X-89/176, July 1989.

20. "An Interlaboratory Comparison of an SW-846 Method for the Analysis of the Chlorinated Phenoxyacid Herbicides by LC/MS", EPA/600/X-90/133, June 1990.

21. Somasundaram, L., and J.R. Coates, Ed., "Pesticide Transformation Products Fate and Significance in the Environment", ACS Symposium Series 459, Ch. 13, 1991.

22. Single-Laboratory Evaluation of Carbamates, APPL, Inc., Fresno, CA.

23. "Interlaboratory Calibration Study of a Thermospray-Liquid Chromatography/ Mass Spectrometry (TS-LC/MS) Method for Selected Carbamate Pesticides", EPA/600/X-92/102, August 1992.

24. Markell, C., "3M Data Submission to EPA," letter to B. Lesnik, June 27, 1995.

TABLE 1

RECOMMENDED HPLC CHROMATOGRAPHIC CONDITIONS

Analytes	Initial Mobile Phase (%)	Initial Time (min)	Final Gradient (linear)	Final Mobile Phase (%)	Time (min)
Organophosphorus Compounds	50/50 (water/methanol)	0	10	100 (methanol)	5
Azo Dyes	50/50 (Water/CH_3CN)	0	5	100 (CH_3CN)	5
Tris(2,3-dibromopropyl) phosphate	50/50 (water/methanol)	0	10	100 (methanol)	5
Chlorinated phenoxyacid compounds	75/25 (0.1 M NH_4 acetate in 1% acetic acid/ methanol)	2	15	40/60 (0.1 M NH_4 acetate in 1% acetic acid/ methanol)	
	40/60 (0.1 M Ammonium acetate in 1% acetic acid/ methanol)	3	5	75/25 (0.1 M Ammonium acetate in 1% acetic acid/ methanol)	10

TABLE 2

RECOMMENDED HPLC CHROMATOGRAPHIC CONDITIONS FOR CARBAMATES

	Time (min)	Mobile phase A (percent)	Mobile phase B (percent)
Option A	0	95	5
	30	20	80
	35	0	100
	40	95	5
	45	95	5

A = 5 mM ammonium acetate with 0.1 M acetic acid, and

B = methanol, with optional post-column addition of 0.5 M ammonium acetate

	Time (min)	Mobile phase A (percent)	Mobile phase B (percent)
Option B	0	95	5
	30	0	100
	35	0	100
	40	95	5
	45	95	5

A = water with 0.1 M ammonium acetate with 1% acetic acid

B = methanol with 0.1 M ammonium acetate with 1% acetic acid, with optional post-column addition of 0.1 M ammonium acetate.

TABLE 3

COMPOUNDS AMENABLE TO THERMOSPRAY MASS SPECTROMETRY

Disperse Azo Dyes	Alkaloids
Methine Dyes	Aromatic ureas
Arylmethane Dyes	Amides
Coumarin Dyes	Amines
Anthraquinone Dyes	Amino acids
Xanthene Dyes	Organophosphorus Compounds
Flame retardants	Chlorinated Phenoxyacid Compounds
Carbamates	

TABLE 4

PRECISION AND ACCURACY COMPARISONS OF MS AND MS/MS WITH HPLC/UV FOR ORGANIC-FREE REAGENT WATER SPIKED WITH DISPERSE RED 1

	Percent Recovery			
	HPLC/UV	MS	CAD	SRM
Spike 1	82.2 ± 0.2	92.5 ± 3.7	87.6 ± 4.6	95.5 ± 17.1
Spike 2	87.4 ± 0.6	90.2 ± 4.7	90.4 ± 9.9	90.0 ± 5.9
RPD	6.1%	2.5%	3.2%	5.9%

Data from Reference 16.

TABLE 5

PRECISION AND ACCURACY COMPARISONS OF MS AND MS/MS WITH HPLC/UV FOR MUNICIPAL WASTEWATER SPIKED WITH DISPERSE RED 1

	Percent Recovery		
	HPLC/UV	MS	CAD
Spike 1	93.4 ± 0.3	102.0 ± 31	82.7 ± 13
Spike 2	96.2 ± 0.1	79.7 ± 15	83.7 ± 5.2
RPD	3.0%	25%	1.2%

Data from Reference 16.

TABLE 6

RESULTS FROM ANALYSES OF ACTIVATED SLUDGE PROCESS WASTEWATER

	Recovery of Disperse Red 1 (mg/L)		
	HPLC/UV	MS	CAD
5 mg/L Spiking Concentration			
1	0.721 ± 0.003	0.664 ± 0.030	0.796 ± 0.008
1-D	0.731 ± 0.021	0.600 ± 0.068	0.768 ± 0.093
2	0.279 ± 0.000	0.253 ± 0.052	0.301 ± 0.042
3	0.482 ± 0.001	0.449 ± 0.016	0.510 ± 0.091
RPD	1.3%	10.1%	3.6%
0 mg/L Spiking Concentration			
1	0.000	0.005 ± 0.0007	<0.001
1-D	0.000	0.006 ± 0.001	<0.001
2	0.000	0.002 ± 0.0003	<0.001
3	0.000	0.003 ± 0.0004	<0.001
RPD	--	18.2%	--

Data from Reference 16.

TABLE 7

CALIBRATION MASSES AND % RELATIVE ABUNDANCES OF PEG 400

Mass	% Relative Abundance[a]
18.0	32.3
35.06	13.5
36.04	40.5
50.06	94.6
77.04	27.0
168.12	5.4
212.14	10.3
256.17	17.6
300.20	27.0
344.22	45.9
388.25	64.9
432.28	100
476.30	94.6
520.33	81.1
564.35	67.6
608.38	32.4
652.41	16.2
653.41	4.1
696.43	8.1
697.44	2.7

[a] Intensities are normalized to mass 432.

TABLE 8

CALIBRATION MASSES AND % RELATIVE ABUNDANCES OF PEG 600

Mass	% Relative Abundance[a]
18.0	4.7
36.04	11.4
50.06	64.9
77.04	17.5
168.12	9.3
212.14	43.9
256.17	56.1
300.20	22.8
344.22	28.1
388.25	38.6
432.28	54.4
476.30	64.9
520.33	86.0
564.35	100
608.38	63.2
652.41	17.5
653.41	5.6
696.43	1.8

[a] Intensities are normalized to mass 564.

TABLE 9

RETENTION TIMES AND THERMOSPRAY MASS SPECTRA
OF ORGANOPHOSPHORUS COMPOUNDS

Compound	Retention Time (min)	Mass (% Relative Abundance)[a]
Monocrotophos	1:09	241 (100), 224 (14)
Trichlorfon	1:22	274 (100), 257 (19), 238 (19)
Dimethoate	1:28	230 (100), 247 (20)
Dichlorvos	4:40	238 (100), 221 (40)
Naled	9:16	398 (100), 381 (23), 238 (5), 221, (2)
Fensulfothion	9:52	326 (10), 309 (100)
Parathion methyl	10:52	281 (100), 264 (8), 251 (21), 234 (48)
Phorate	13:30	278 (4), 261 (100)
Disulfoton	13:55	292 (10), 275 (100)
Merphos	18:51	315 (100), 299 (15)

[a] For molecules containing Cl, Br and S, only the base peak of the isotopic cluster is listed.

Data from Reference 17.

TABLE 10

SINGLE OPERATOR ACCURACY AND PRECISION FOR LOW CONCENTRATION DRINKING WATER, LOW CONCENTRATION SOIL, MEDIUM CONCENTRATION DRINKING WATER, MEDIUM CONCENTRATION SEDIMENT

Matrix	Compound	Mean Rec. (%)	Std. Dev.	Spike Conc.	Recovery Range (%)	# Analyses
Low conc. drinking water	Dimethoate	70	7.7	5	85 - 54	15
(µg/L)	Dichlorvos	40	12	5	64 - 14	15
	Naled	0.5	1.0	5	2 - 0	15
	Fensulfothion	112	3.3	5	119 - 106	15
	Parathion methyl	50	28	10	105 - 0	15
	Phorate	16	35	5	86 - 0	15
	Disulfoton	3.5	8	5	19 - 0	15
	Merphos	237	25	5	287 - 187	15
Low conc. soil	Dimethoate	16	4	50	24 - 7	15
(µg/kg)	Dichlorvos	ND		50		15
	Naled	ND		50		15
	Fensulfothion	45	5	50	56 - 34	15
	Parathion methyl	ND		100		15
	Phorate	78	15	50	109 - 48	15
	Disulfoton	36	7	50	49 - 22	15
	Merphos	118	19	50	155 - 81	15

TABLE 10
(continued)

Matrix	Compound	Mean Rec. (%)	Std. Dev.	Spike Conc.	Recovery Range (%)	# Analyses
Medium conc. drinking water	Dimethoate	52	4	50	61 - 43	12
(µg/L)	Dichlorvos	146	29	50	204 - 89	12
	Naled	4	3	50	9 - 0	12
	Fensulfothion	65	7	50	79 - 51	12
	Parathion methyl	85	24	100	133 - 37	12
	Phorate	10	15	50	41 - 0	12
	Disulfoton	2	1	50	4 - 0	12
	Merphos	101	13	50	126 - 75	12
Medium conc. sediment	Dimethoate	74	8.5	2	91 - 57	15
(mg/kg)	Dichlorvos	166	25	2	216 - 115	15
	Naled	ND		2		15
	Fensulfothion	72	8.6	2	90 - 55	15
	Parathion methyl	84	9	3	102 - 66	15
	Phorate	58	6	2	70 - 46	15
	Disulfoton	56	5	2	66 - 47	15
	Merphos	78	4	2	86 - 70	12

Data from Reference 17.

TABLE 11

SINGLE OPERATOR ACCURACY AND PRECISION FOR TRIS-BP IN MUNICIPAL WASTE WATER, DRINKING WATER, CHEMICAL SLUDGE

Compound	Matrix	Mean Rec. (%)	Std. Dev.	Spike Conc.	Recovery Range (%)	# Analyses
Tris-BP	Municipal wastewater	25	8.0	2	41 - 9.0	15
	Drinking water	40	5.0	2	50 - 30	12
	Chemical sludge	63	11	100	84 - 42	8

Data from Reference 18.

TABLE 12

SINGLE LABORATORY OPERATOR ACCURACY AND PRECISION
FOR THE CHLORINATED PHENOXYACID HERBICIDES

Compound	Mean Recovery %	Std. Dev.	Spike Conc.	Recovery Range (%)	# Analyses
LOW LEVEL DRINKING WATER			µg/L		
Dicamba	63	22	5	86 - 33	9
2,4-D	26	13	5	37 - 0	9
MCPA	60	23	5	92 - 37	9
MCPP	78	21	5	116 - 54	9
Dichlorprop	43	18	5	61 - 0	9
2,4,5-T	72	31	5	138 - 43	9
Silvex	62	14	5	88 - 46	9
2,4-DB	29	24	5	62 - 0	9
Dinoseb	73	11	5	85 - 49	9
Dalapon	ND	ND	5	ND	9
2,4-D,ester	73	17	5	104 - 48	9
HIGH LEVEL DRINKING WATER					
Dicamba	54	30	50	103 - 26	9
2,4-D	60	35	50	119 - 35	9
MCPA	67	41	50	128 - 32	9
MCPP	66	33	50	122 - 35	9
Dichlorprop	66	33	50	116 - 27	9
2,4,5-T	61	23	50	99 - 44	9
Silvex	74	35	50	132 - 45	9
2,4-DB	83	25	50	120 - 52	9
Dinoseb	91	10	50	102 - 76	9
Dalapon	43	9.6	50	56 - 31	9
2,4-D,ester	97	19	50	130 - 76	9

TABLE 12
(continued)

Compound	Mean Recovery %	Std. Dev.	Spike Conc.	Recovery Range (%)	# Analyses
LOW LEVEL SAND			µg/g		
Dicamba	117	26	0.1	147 - 82	10
2,4-D	147	23	0.1	180 - 118	10
MCPA	167	79	0.1	280 - 78	10
MCPP	142	39	0.1	192 - 81	10
Dichlorprop	ND	ND	0.1	ND	10
2,4,5-T	134	27	0.1	171 - 99	10
Silvex	121	23	0.1	154 - 85	10
2,4-DB	199	86	0.1	245 - 0	10
Dinoseb	76	74	0.1	210 - 6	10
Dalapon	ND	ND	0.1	ND	10
2,4-D,ester	180	58	0.1	239 - 59	7
HIGH LEVEL SAND			µg/g		
Dicamba	153	33	1	209 - 119	9
2,4-D	218	27	1	276 - 187	9
MCPA	143	30	1	205 - 111	9
MCPP	158	34	1	226 - 115	9
Dichlorprop	92	37	1	161 - 51	9
2,4,5-T	160	29	1	204 - 131	9
Silvex	176	34	1	225 - 141	9
2,4-DB	145	22	1	192 - 110	9
Dinoseb	114	28	1	140 - 65	9
Dalapon	287	86	1	418 - 166	9
2,4-D,ester	20	3.6	1	25 - 17	7

TABLE 12
(continued)

Compound	Mean Recovery %	Std. Dev.	Spike Conc.	Recovery Range (%)	# Analyses
LOW LEVEL MUNICIPAL ASH			µg/g		
Dicamba	83	22	0.1	104 - 48	9
2,4-D	ND	ND	0.1	ND	9
MCPA	ND	ND	0.1	ND	9
MCPP	ND	ND	0.1	ND	9
Dichlorprop	ND	ND	0.1	ND	9
2,4,5-T	27	25	0.1	60 - 0	9
Silvex	68	38	0.1	128 - 22	9
2,4-DB	ND	ND	0.1	ND	9
Dinoseb	44	13	0.1	65 - 26	9
Dalapon	ND	ND	0.1	ND	9
2,4-D,ester	29	23	0.1	53 - 0	6
HIGH LEVEL MUNICIPAL ASH			µg/g		
Dicamba	66	21	1	96 - 41	9
2,4-D	8.7	4.8	1	21 - 5	9
MCPA	3.2	4.8	1	10 - 0	9
MCPP	10	4.3	1	16 - 4.7	9
Dichlorprop	ND	ND	1	ND	9
2,4,5-T	2.9	1.2	1	3.6 - 0	9
Silvex	6.0	3.1	1	12 - 2.8	9
2,4-DB	ND	ND	1	ND	9
Dinoseb	16	6.8	1	23 - 0	9
Dalapon	ND	ND	1	ND	9
2,4-D,ester	1.9	1.7	1	6.7 - 0	6

Source: Reference 19.
All recoveries are in negative ionization mode, except for 2,4-D, ester.
ND = Not Detected.

TABLE 13

MULTI-LABORATORY ACCURACY AND PRECISION DATA
FOR THE CHLORINATED PHENOXYACID HERBICIDES

Compound	Spiking Concentration	Mean (% Recovery)[a]	RSD[b]
2,4,5-T	500 mg/L	90	23
2,4,5-T,butoxy ester		90	29
2,4-D		86	17
2,4-DB		95	22
Dalapon		83	13
Dicamba		77	25
Dichlorprop		84	20
Dinoseb		78	15
MCPA		89	11
MCPP		86	12
Silvex		96	27
2,4,5-T	50 mg/L	62	68
2,4,5-T,butoxy ester		85	9
2,4-D		64	80
2,4-DB		104	28
Dalapon		121	99
Dicamba		90	23
Dichlorprop		96	15
Dinoseb		86	57
MCPA		96	20
MCPP		76	74
Silvex		65	71

TABLE 13
(continued)

Compound	Spiking Concentration	Mean (% Recovery)[a]	RSD[b]
2,4,5-T	5 mg/L	90	28
2,4,5-T,butoxy ester		99	17
2,4-D		103	31
2,4-DB		96	21
Dalapon		150	4
Dicamba		105	12
Dichlorprop		102	22
Dinoseb		108	30
MCPA		94	18
MCPP		98	15
Silvex		87	15

[a] Mean of duplicate data from 3 laboratories.
[b] Relative standard deviation of duplicate data from 3 laboratories.
Data from Reference 20.

TABLE 14

SINGLE-LABORATORY EVALUATION OF AVERAGE RECOVERY AND PRECISION DATA FOR WATER[c]

Analyte	Average % Recovery[b]	Standard Deviation	%RSD
Aldicarb sulfoxide	7.6	2.8	37.0
Aldicarb sulfone	56.0	27.1	48.5
Oxamyl[a]	38.9	17.9	45.9
Methomyl	52.0	19.6	37.7
3-Hydroxycarbofuran[a]	22.2	9.3	41.7
Fenuron	72.5	22.0	30.3
Benomyl/Carbendazim	47.3	14.7	31.0
Aldicarb	81.0	13.7	16.9
Aminocarb	109	38.3	35.1
Carbofuran	85.5	10.0	11.7
Propoxur	79.1	13.7	17.3
Monuron	91.8	11.3	12.3
Bromacil	87.6	12.1	13.8
Tebuthiuron	87.1	9.0	10.3
Carbaryl	82.1	13.5	16.5
Fluometuron	84.4	8.3	9.8
Propham	80.7	13.8	17.1
Propachlor	84.3	10.0	11.9
Diuron	90.8	14.1	15.6
Siduron	88.0	9.5	10.8
Methiocarb	93.3	12.8	13.8
Barban	88.1	11.2	12.7
Linuron	87.1	16.8	19.3
Chloropropham	94.9	15.3	16.1
Mexacarbate	79.8	12.9	16.2
Chloroxuron	106	24.9	23.5
Neburon	85.3	12.6	14.8

[a] Values generated from internal response factor calculations.

[b] Nine spikes were performed at three concentrations. The concentrations for Aldicarb sulfoxide, Barban, Chloropropham, and Mexacarbate spike levels were at 25 µg/L, 50 µg/L, and 100 µg/L. All other analyte concentrations were 5 µg/L, 10 µg/L, and 20 µg/L. One injection was disregarded as an outlier. The total number of spikes analyzed was 26.

[c] Data from Reference 22.

TABLE 15

SINGLE-LABORATORY EVALUATION OF AVERAGE RECOVERY AND PRECISION DATA FOR SOIL[b]

Analyte	Average % Recovery[a]	Standard Deviation	%RSD
Aldicarb sulfoxide	66.9	31.3	46.7
Aldicarb sulfone	162	51.4	31.7
Oxamyl	78.9	46.1	58.5
Methomyl	84.9	25.8	30.4
3-Hydroxycarbofuran	105	36.3	34.5
Fenuron	91.9	16.7	18.1
Benomyl/Carbendazim	95.6	18.2	19.0
Aldicarb	97.9	17.0	17.4
Aminocarb	133	44.7	33.6
Carbofuran	109	14.4	13.2
Propoxur	104	16.5	15.9
Monuron	101	12.4	12.3
Bromacil	100	9.0	9.0
Tebuthiuron	104	11.9	11.5
Carbaryl	102	15.5	15.2
Fluometuron	94.5	15.7	16.7
Propham	92.8	12.0	12.9
Propachlor	94.6	10.3	10.9
Diuron	107	17.4	16.2
Siduron	100	12.0	12.0
Methiocarb	107	14.2	13.2
Barban	92.3	15.6	16.9
Linuron	104	13.6	13.1
Chloropropham	105	9.3	8.9
Mexacarbate	77.2	9.8	12.7
Chloroxuron	121	27.3	22.5
Neburon	92.1	16.5	17.9

[a] Nine spikes were performed at three concentrations. The concentrations for Aldicarb sulfoxide, Barban, Chloropropham, and Mexacarbate spike levels were at 0.625 µg/g, 1.25 µg/g, and 2.5 µg/g. All other analyte concentrations were 0.125 µg/g, 0.25 µg/g, and 0.50 µg/g. One injection was disregarded as an outlier. The total number of spikes analyzed was 26.

[b] Data from Reference 22.

TABLE 16

MULTI-LABORATORY EVALUATION OF METHOD ACCURACY
(AFTER OUTLIER REMOVAL)[d]

	Percent Recovery		
Analyte	High-Concentration Samples[a]	Medium-Concentration Samples[b]	Low-Concentration Samples[c]
Aldicarb	98.7	110	52.0
Bendiocarb	81.4	95.0	52.0
Carbaryl	92.0	108	62.0
Carbendazim	125	138	128
Carbofuran	87.8	92.3	72.0
Diuron	79.9	98.8	66.0
Linuron	84.8	93.0	82.0
Methomyl	93.3	90.8	90.0
Oxamyl	83.8	88.0	98.0

[a] Three replicates per laboratory; eight to nine laboratories (per Table 26 of Reference 23). The true concentration is 90 mg/L per compound, except Carbendazim at 22.5 mg/L.

[b] Two replicates per laboratory; eight to nine laboratories (per Table 26 of Reference 23). The true concentration is 40 mg/L per compound except Carbendazim at 10 mg/L.

[c] Three replicates per laboratory; eight to nine laboratories (per Table 26 of Reference 23). The true concentration is 5 mg/L per compound, except Carbendazim at 1.25 mg/L.

[d] Data from Reference 23.

TABLE 17

MULTI-LABORATORY EVALUATION OF METHOD PRECISION (AFTER OUTLIER REMOVAL)[a]

Analyte	High Concentration					Medium Concentration					Low Concentration				
	Avg.	s_r	s_R	$\%RSD_R$	$\%RSD_R$	Avg.	s_r	s_R	$\%RSD_r$	$\%RSD_R$	Avg	s_r	s_R	$\%RSD_r$	$\%RSD_R$
Aldicarb	88.8	11.4	34.4	12.9	38.8	44.1	7.7	17.0	17.5	38.5	2.6	0.9	2.6	33.1	98.2
Bendiocarb	73.3	16.1	39.3	21.9	53.6	38.0	6.6	16.6	17.3	43.7	2.6	0.6	1.6	21.3	61.9
Carbaryl	82.8	11.7	34.0	14.2	41.1	43.1	3.0	15.7	7.0	36.4	3.1	0.7	2.3	23.3	75.8
Carbendazim	28.1	5.6	15.3	19.9	54.4	13.8	1.4	8.9	10.4	64.2	1.6	0.4	1.1	26.1	68.2
Carbofuran	79.0	16.7	35.2	21.2	44.5	36.9	5.0	16.3	13.6	44.3	3.6	0.9	3.3	25.2	91.6
Diuron	71.9	13.1	26.1	18.2	36.3	39.5	2.6	11.8	6.5	29.8	3.3	0.5	2.6	16.2	77.9
Linuron	76.3	8.3	32.5	10.9	42.6	37.2	3.9	13.4	10.5	35.9	4.1	0.6	2.1	15.7	51.4
Methomyl	84.0	10.8	29.4	12.9	35.0	36.3	2.8	15.0	7.8	41.2	4.5	0.7	4.1	15.3	92.9
Oxamyl	75.5	12.4	37.0	16.4	49.1	35.2	3.7	20.8	10.4	59.1	4.9	0.5	4.6	9.7	93.6
Average				16.5	43.9				11.2	43.7				20.7	79.1
Std. Dev.				4.0	7.1				4.1	11.2				7.1	16.3

s_r and s_R are the standard deviations for repeatability and reproducibility, respectively. RSD_r and RSD_R are the corresponding relative standard deviations for repeatability and reproducibility, respectively. The units for average, s_r and s_R are mg/L.

[a] Data from Reference 23.

TABLE 18

SINGLE LABORATORY RECOVERY DATA FOR SOLID-PHASE EXTRACTION OF CHLORINATED HERBICIDES FROM SPIKED TCLP BUFFERS

		Buffer 1		Buffer 2	
Compound	Spike Level (µg/L)	Recovery (%)	RSD	Recovery (%)	RSD
2,4-D	5,000	91	2	79	6
2,4,5-TP	500	93	9	92*	2*
2,4-D	20,000	100	3	99*	1*
2,4,5-TP	2000	103*	2*	78	7

Except where noted with an asterisk, all results are from seven replicates. Those marked with an asterisk are from three replicates.

Data are from Reference 24.

FIGURE 1
SCHEMATIC OF THE THERMOSPRAY PROBE AND ION SOURCE

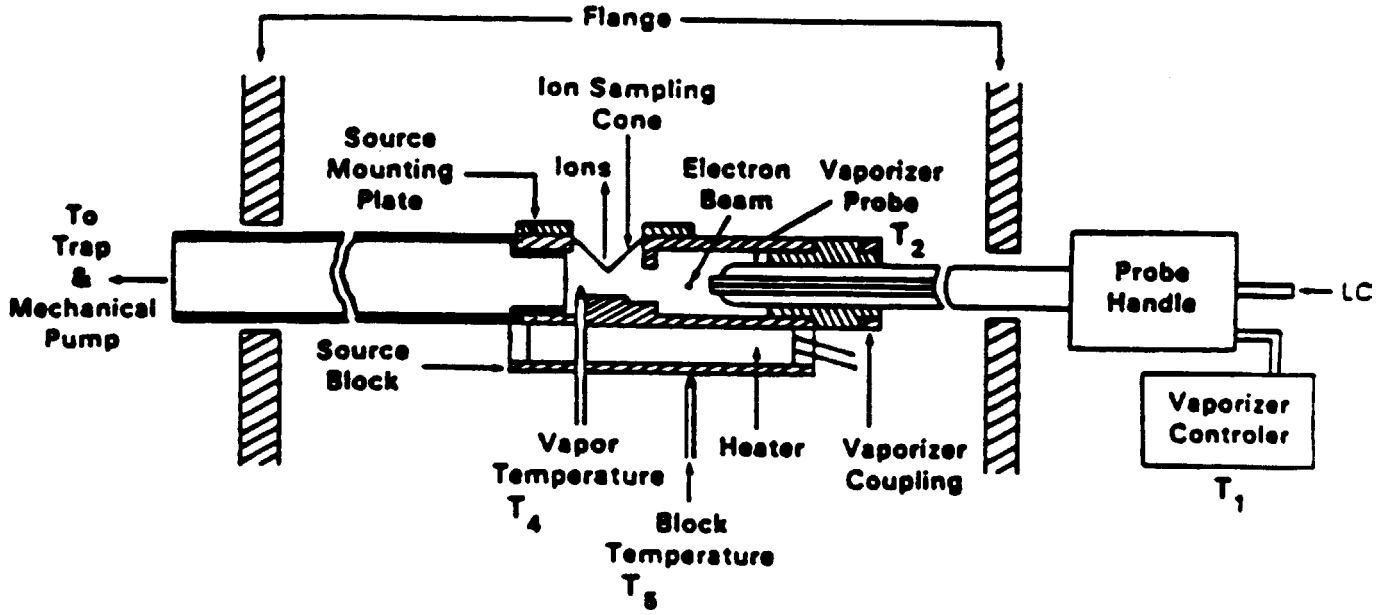


FIGURE 2
THERMOSPRAY SOURCE WITH WIRE-REPELLER
(High sensitivity configuration)

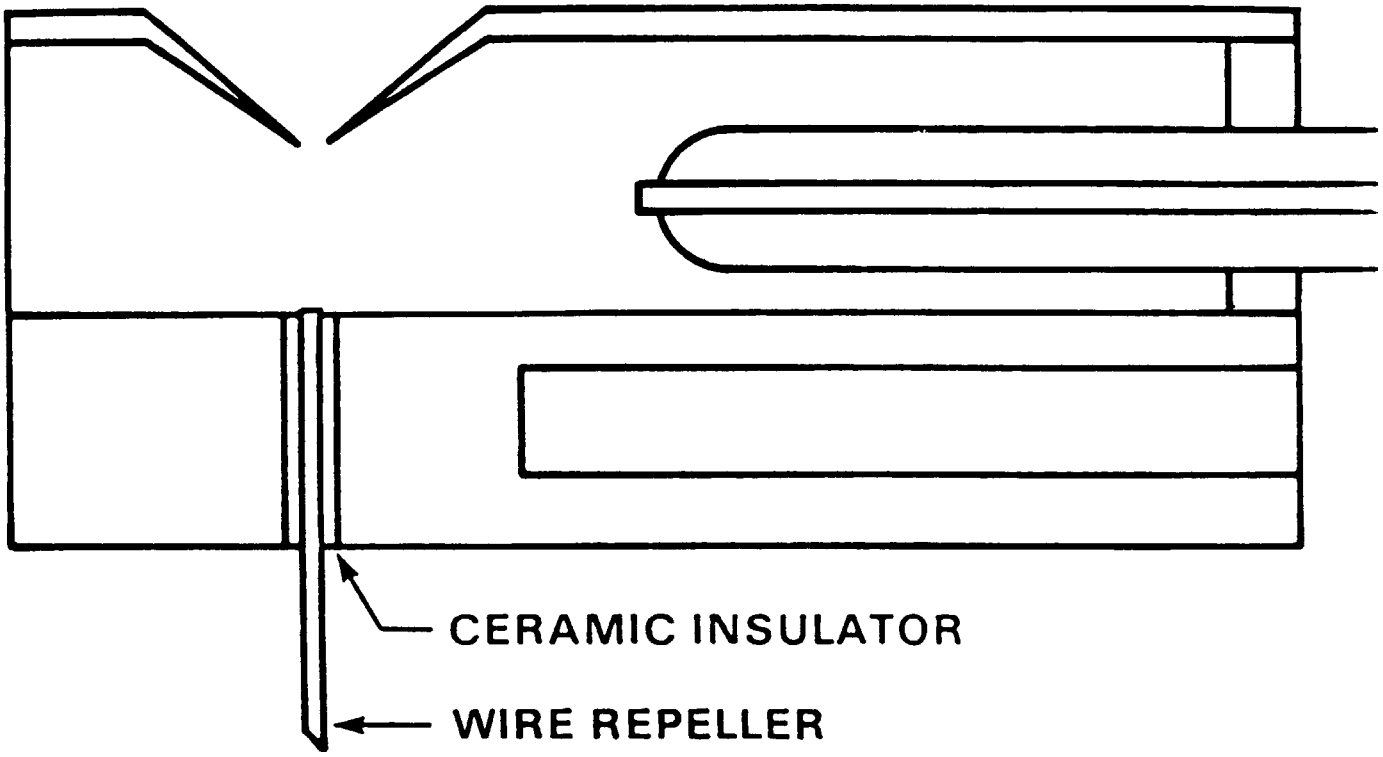
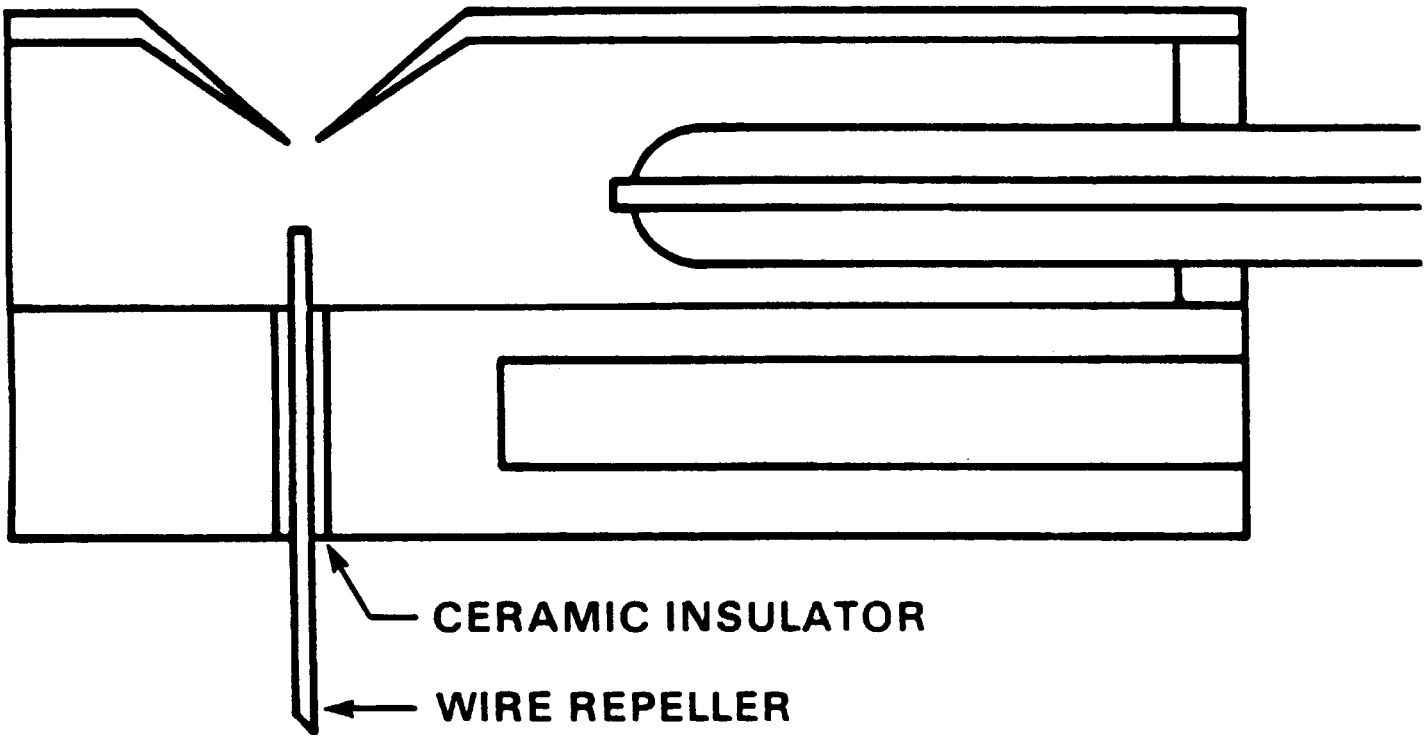
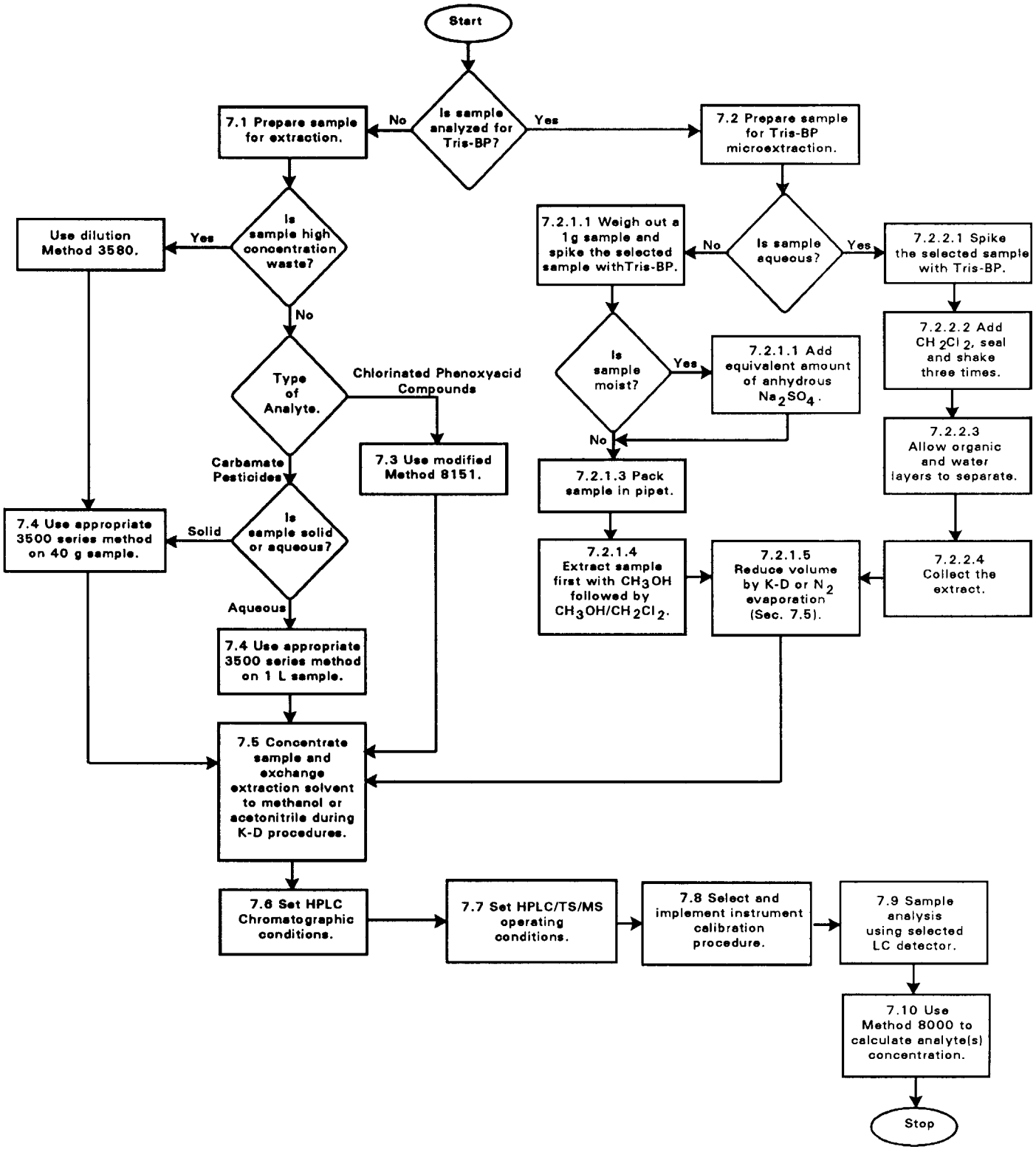


FIGURE 3
THERMOSPRAY SOURCE WITH WIRE-REPELLER
(CAD configuration)




Start
Is sample analyzed for Tris-BP?
No
Yes
7.1 Prepare sample for extraction.
7.2 Prepare sample for Tris-BP microextraction.
Is sample high concentration waste?
Yes
Use dilution Method 3580.
No
Type of Analyte.
Chlorinated Phenoxyacid Compounds
7.3 Use modified Method 8151.
Carbamate Pesticides
Is sample solid or aqueous?
Solid
7.4 Use appropriate 3500 series method on 40 g sample.
Aqueous
7.4 Use appropriate 3500 series method on 1 L sample.
7.2.1.1 Weigh out a 1g sample and spike the selected sample withTris-BP.
Is sample aqueous?
No
Yes
7.2.2.1 Spike the selected sample with Tris-BP.
Is sample moist?
Yes
7.2.1.1 Add equivalent amount of anhydrous Na_2SO_4.
No
7.2.2.2 Add CH_2Cl_2, seal and shake three times.
7.2.2.3 Allow organic and water layers to separate.
7.2.1.3 Pack sample in pipet.
7.2.1.4 Extract sample first with CH_3OH followed by CH_3OH/CH_2Cl_2.
7.2.1.5 Reduce volume by K-D or N_2 evaporation (Sec. 7.5).
7.2.2.4 Collect the extract.
7.5 Concentrate sample and exchange extraction solvent to methanol or acetonitrile during K-D procedures.
7.6 Set HPLC Chromatographic conditions.
7.7 Set HPLC/TS/MS operating conditions.
7.8 Select and implement instrument calibration procedure.
7.9 Sample analysis using selected LC detector.
7.10 Use Method 8000 to calculate analyte(s) concentration.
Stop